

STABILIZER COMPOSITIONS

The invention relates to stabilizer compositions for stabilizing polyethylene-based thermoplastic polymers in processing.

During processing into articles, polymers are subjected to high temperatures and pressures which can have an adverse effect on the molecular weight and physical properties of the polymers and on the appearance of the finished articles made from these polymers. Therefore, there is a need for antioxidant and color stabilizing additives which minimize oxidation and discoloration.

United States Patent No. 4 806 580 discloses stabilizer mixtures for stabilizing plastics material, e.g. polypropylene, in processing, containing (a) a chroman derivative and (b) an organic phosphite or phosphonite in a weight ratio of a:b of 1:5 to 1:14.

European Patent Application 0 542 108 discloses a stabilizing mixture for plastics materials containing polyethylene, comprising (a) a tocopherol compound and (b) a phosphorus- or sulphur-containing secondary antioxidant in a weight ratio of a:b of 1:1.4 to 1:5. The corresponding disclosure exists in the article of S.F. Laermer and P.F. Zambetti published in the Journal of Plastic Film & Sheeting, volume 8, 1992, pages 228 to 248. This article further describes a mixture of α -tocopherol, "Irganox (trade mark) 1010" (a sterically hindered phenol), and "Irgafos 168" (a phosphite) in the weight ratio of 1:1.4 for the stabilization of polypropylene.

The article of S.S. Young, S.F. Laermer and P.F. Zambetti published in the Journal of Plastic Film & Sheeting, volume 11, 1995, pages 126 to 142, demonstrates that α -tocopherol formulations can replace phenol/phosphite combinations as the primary antioxidant system, or the α -tocopherol formulations can simply replace the phosphite portion to achieve better performance.

German Patent No. 26 60 746 discloses the use of symmetrical triarylphosphites in combination with sterically hindered phenolic antioxidants in the stabilization of polyolefins.

It is the object of the present invention to provide an improved stabilizer composition for the stabilization of polyethylene-based thermoplastic polymers, such that both processing stability and color of the final products are improved.

5 This object is achieved with the stabilizer composition as hereinunder described. It has surprisingly been found that relatively small additions of α -tocopherol to known additive systems for polyethylene-based polymers, composed of a phenolic antioxidant and a phosphorus based secondary antioxidant, results in an unexpected synergistic effect. This stabilizer composition according to the invention comprising at least one member of three known additive classes significantly outperforms the additive systems that are known in the art.

Accordingly, the present invention provides a stabilizer composition comprising

- a) at least one sterically hindered phenol,
- b) at least one phosphorus-containing secondary antioxidant, and
- c) at least one tocopherol compound

wherein the weight ratio of component (a) to component (b) is from 2:1 to 1:4 and the weight ratio of component (a) to component (c) is from 2:1 to 10:1,

20 for the stabilization of polyethylene-based thermoplastic polymers against degradation, crosslinking and/or discoloration due to the exposure to heat or light, especially in the presence of oxygen.

The preferred weight ratio of component (a) to component (b) is 1:1 and that of component (a) to component (c) is 5:1.

The term "tocopherol compound" refers to any compound having the basic tocopherol structure of the vitamin E group. The preferred tocopherol compound as component (a) in the stabilizer composition according to the present invention is α -tocopherol (5,7,8-trimethyl-tocol).

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As used herein, the term "sterically hindered phenol" refers to those compounds that are preferably derived from 2,6-di-tert.-butyl-phenol, 2-tert.-butyl-6-methylphenol, 2-tert.-butyl-5-

methylphenol or other hindered phenols. Preferred examples of such compounds are 2,2'-
 Bis[3,5-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl-1,3-propanediyl-
 3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoate; octadecyl-3,5-bis(1,1-dimethylethyl)-
 4-hydroxybenzene-propanoate; 1,3,5tris[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]-
 1,3,5-triazine-2,4,6(1H,3H,5H)-trione; 4,4',4''-[2,4,6-trimethyl-1,3,5-benzenetriyl]tris-
 (methylene)]tris[2,6-bis(1,1-dimethylethyl)-phenol; Ethanediyl-3,5-bis(1,1-dimethylethyl)-4-
 hydroxy-thiodi-2,1-benzenepropanoate; 2:1 calcium salt of monoethyl-[[3,5-bis(1,1-
 dimethylethyl)-4-hydroxyphenyl]methyl]-phosphonic acid ester; 2-[3-[3,5-bis(1,1-
 dimethylethyl)-4-hydroxy-phenyl]-1-oxo-propyl]hydrazide-3,5-bis(1,1-dimethylethyl)-4-
 hydroxy-benzenepropanoic acid; 2,2'-oxamido-bis-[ethyl-3-(3,5-di-tert.butyl-4-
 hydroxyphenyl)propionate] or mixtures thereof.

As also used herein, the term "phosphorus-containing secondary antioxidant" refers to
 compounds being hydroperoxide decomposers, i.e. compounds having the ability to react with
 hydroperoxides to yield non-radical products, essentially decomposing hydroperoxides into
 stable by-products. Examples of such compounds are triesters of phosphorous acid (phosphites)
 and diesters of phosphorous acid (phosphonites). Preferred specific members of the phosphorus-
 containing secondary antioxidants are Triphenylphosphite, Trisisodecylphosphite;
 Tris(nonylphenyl)phosphite; Distearyl pentaerythritol diphosphite; 2,4,6-tri-tert.-butyl-phenyl-2-
 butyl-2-ethyl-1,3-propanediol phosphite; Bis(2,4-di-tert.-butylphenyl)-pentaerythrityl
 diphosphite; 2,2',2''-nitrilo triethyl-tris[3,3',5,5'-tetra-tert.-butyl-1,1'-biphenyl-2,2'-
 diyl]phosphite; Bis[2,4-di-tert.-butyl-6-methyl-phenyl]ethyl phosphite; 2,2'-Ethylidene-bis-(4,6-
 di-tert.-butylphenyl)fluorophosphite; Tris-(2,4-di-tert.-butylphenyl)phosphite; the 4,6-di-tert.-
 butyl-m-cresol condensation products with the Friedel-Crafts-reaction products of biphenyl and
 phosphorus trichloride; Tetrakis [2,4-di-tert.-butylphenyl]-4,4'-biphenylenediphosphonite; the
 condensation products of 2,4-di-tert.-butylphenol with the Friedel-Crafts-reaction product of
 biphenyl and PCl_3 .

The term "polyethylene-based thermoplastic polymer" refers to all types of homo- and
 copolymers of ethylene, e.g. high density polyethylene, low density polyethylene, linear low
 density polyethylene, ultra low density polyethylene and ultra high molecular weight
 polyethylene or to blends of polyethylene and at least another polymer. Those skilled in the art

will know how to make the different types of copolymers that can be formed with ethylene, including alternating, block and graft copolymers as well as how to make blends of polyethylene with other polymers.

- 5 If in the stabilizer composition according to the present invention more than one compound of component (a), (b) or (c) is present, the definition of the weight ratios always refers to the total amount of component (a), (b) or (c).

The phosphites and phosphonites as well as the sterically hindered phenols disclosed above can be synthesized by techniques well known in the art from known compounds. They are commercially available and their tradenames as well as their chemical structural formulae are summarized in table 1.

The stabilizer composition of the present invention may be produced by simple physical mixing of the compounds (a), (b) and (c) in the desired weight ratio according to known methods. A preferred method is the dry blending of the components resulting in a free-flowing mixture which may be further subjected to a pre-extrusion step in order to achieve homogeneity and easy-to-handle pellets. The process for producing the stabilizer composition is a further aspect of the present invention.

20 A masterbatch composition comprising a stabilizer composition according to the invention and a thermoplastic material which is identical to or compatible with the thermoplastic polymer to be stabilized is similarly an object of the invention. Masterbatch compositions according to the invention comprise 10 to 80% by weight, preferably 5 to 25% by weight of the stabilizer
25 composition and 90% to 20% by weight, preferably 95 to 75% by weight of the afore-mentioned thermoplastic material.

The invention also provides a method for enhancing the processing stability of polyethylene-based thermoplastic polymers comprising - incorporating therein at any convenient state of the
30 processing - a stabilizing quantity of the stabilizer composition. This can be carried out according to known methods and may involve the incorporation of the stabilizer composition as such or in

the form of the above-mentioned masterbatch. Also, the individual components can be incorporated separately in the correct ratio.

The concentration of the stabilizer mixture amounts from 0.001 to 5% , preferably from 0.01 to 1%, more preferably from 0.1 to 0.5% by weight, based on the weight of the polyethylene-based thermoplastic polymers to be stabilized.

The present invention further embraces a stabilized polyethylene-based thermoplastic polymer and any article manufactured therefrom that has been stabilized by the incorporation therein a stabilizing quantity of the stabilizer composition according to the present invention.

Further additives which may be added, if appropriate, include plasticizers, lubricants, emulsifiers, pigments, dyestuffs, nucleating agents, optical brighteners, flameproofing agents, antistatic agents, blowing agents, U.V. absorbers, U.V. quenchers, hindered amine light stabilizers, metal deactivators and several others commonly used.

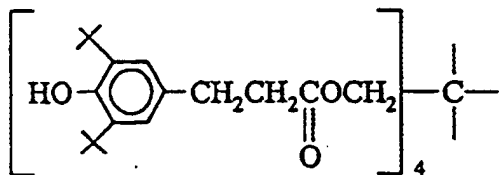
As mentioned above the tradenames, the chemical structural formulae and the chemical names of the components (a) and (b) are listed in table 1.

TABLE 1

Trade names, chemical names and chemical structural formulae of the individual components of the stabilizer composition according to the invention.

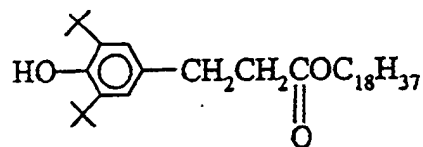
Irganox® 1010 (Ciba-Geigy)

Tetrakis[methylen-3-(3',5')-di-tert.-butyl-4'-hydroxyphenyl]propionate]methane



Irganox®1076 (Ciba-Geigy)

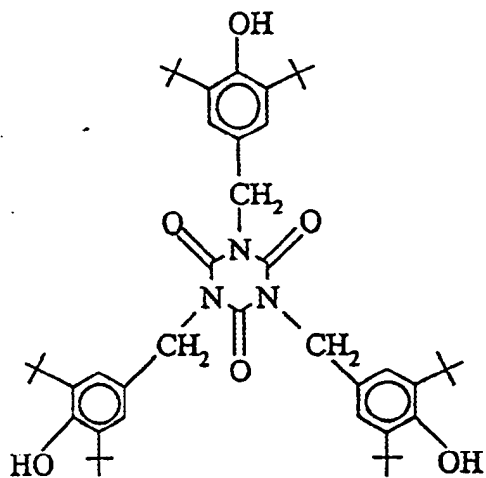
Octadecyl-3,5-bis(1,1-dimethylethyl)-4-hydroxybenzenepropanoate



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Irganox®3114 (Ciba-Geigy)

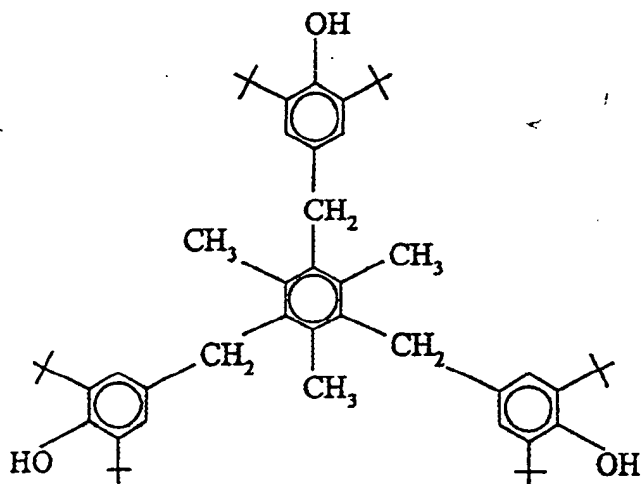
1,3,5-tris[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]-1,3,5-triazine-2,4,6(1H,3H,5H)-trione



Irganox® 1330 (Ciba-Geigy)

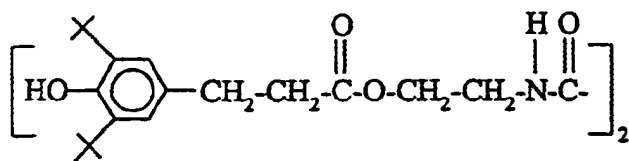
4,4',4''-[(2,4,6-trimethyl-1,3,5-benzenetriyl)tris(methylene)]-tris[2,6-bis(1,1-dimethylethyl)phenol]

5



Naugard® XL-1 (Uniroyal Chemical)

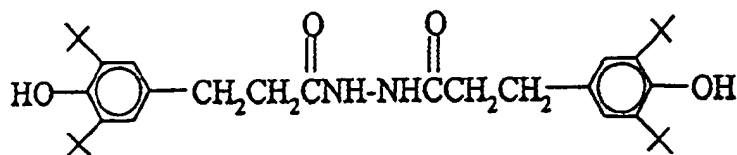
2,2'-oxamido-bis-[ethyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)propionate]



Irganox[®] MD-1024 (Ciba-Geigy)

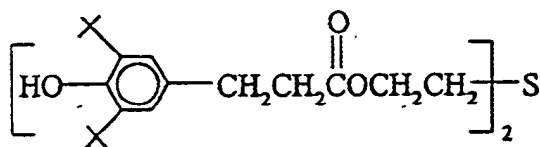
2-[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1-oxopropyl]hydrazide-3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzenepropanoic acid

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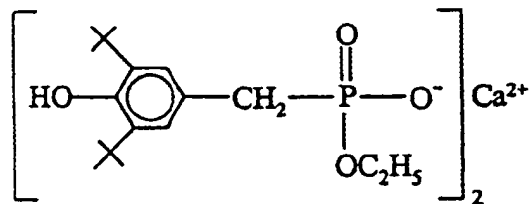
Irganox[®] 1035 (Ciba-Geigy)

Ethanediyyl -3,5-bis(1,1-dimethylethyl)-4-hydroxy-thiodi-2,1-benzenepropanoate



15 Irganox[®] 1425 WL (Ciba-Geigy)

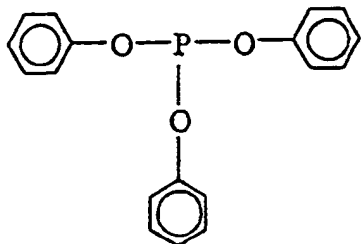
2:1 calcium salt of monoethyl-[[3,5-bis(1,1-dimethylethyl)-4-hydroxy-phenyl]methyl]-phosphonic acid ester



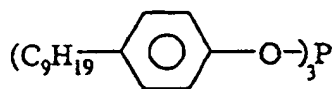
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Weston[®]TPP (General Electric)

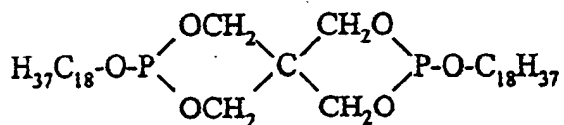
Triphenyl phosphite

Weston[®]TNPP (General Electric)

Tris(nonylphenyl)phosphite

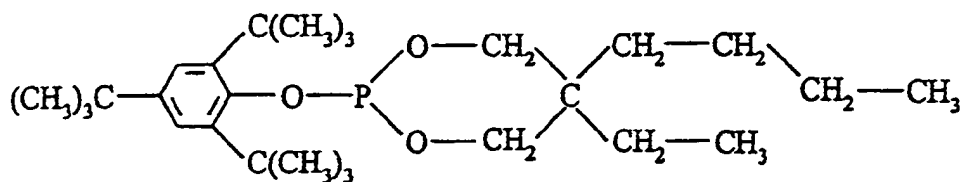
Weston[®]618 (General Electric)

15 Distearyl pentaerythritol Diphosphite



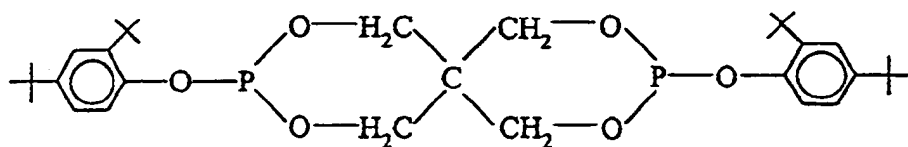
Ultranox® 641 (General Electric)

2,4,6-tri-tert.-butylphenyl-2-butyl-2-ethyl-1,3-propanediol phosphite



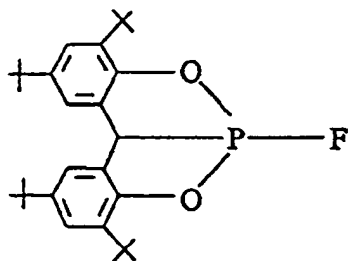
Ultranox® 626 (General Electric)

Bis(2,4-di-tert-butylphenyl)-pentaerythritol-diphosphite



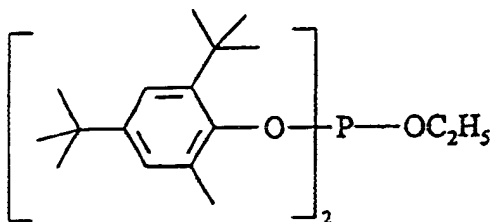
Ethanox 398 (Ethyl Corporation)

2,2'-Ethylidene-bis(4,6-di-tert.-butylphenyl)fluorophosphite



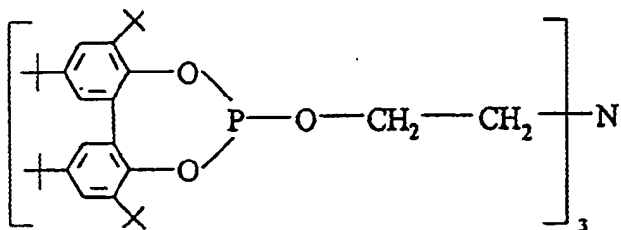
Irgafos®38 (Ciba-Geigy)

Bis[2,4-di-tert.-butyl-6-methylphenyl]ethyl phosphite



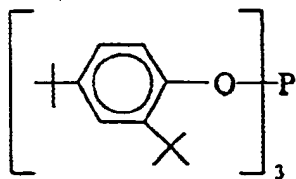
Irgafos®12 (Ciba-Geigy)

2,2',2''-nitro triethyl-tris[3,3',5,5'-tetra-tert.-butyl-1,1'-biphenyl-2,2'-diyl]phosphite



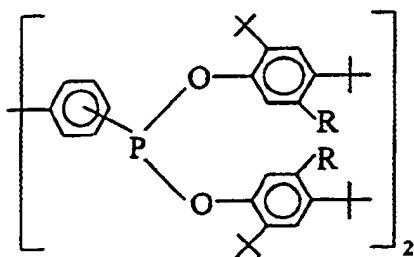
Irgafos®168 (Ciba-Geigy)

15 Tris(2,4-di-tert.-butylphenyl)phosphite



GSY P-101 (Yoshitomi)

Tetrakis[2,4-di-tert.-butyl-5-methyl-phenyl]biphenylene-diphosphonite

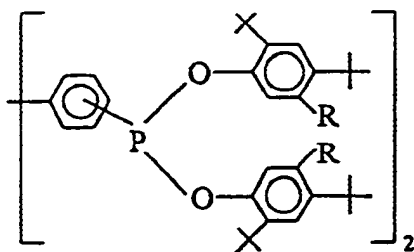
 $R = \text{CH}_3$

Irgafos®P-EPQ (Ciba-Geigy)

Sandostab®P-EPQ (Clariant)

Composed of

- 1) 50-80 parts of Tetrakis(2,4-di-tert.-butylphenyl)-biphenylene-diphosphonite

 $R = \text{H}$

- 2) 10-25 parts of bis(2,4-di-tert.-butylphenyl)biphenylene-monophosphonite
- 3) 10-25 parts of tris(2,4-di-tert.-butylphenyl)phosphite

For avoidance of doubt, in this specification tert.-butyl means tertiary-butyl, $-\text{C}(\text{CH}_3)_3$.

- 20 The following non-limiting examples illustrate the invention in its various aspects. All parts and percentages are expressed by weight.

EXAMPLES

The following types of unstabilized polyethylene are used in the examples described hereinunder:

PE No.	Type of Polyethylene
PE-1	HDPE, prepared with Cr-catalyst, blow molding grade MFI = 0.25 g / 10 min (190°C / 2.16 kg) MFI = 18.96 g / 10 min (190°C / 21.6 kg)
PE-2	HDPE, prepared with Ti-catalyst MFI = 2.4 g / 10 min (190°C / 10 kg)
PE-3	LLDPE, MFI = 1.4 g / 10 min (190°C / 2.16 kg)

The various additives tested are used as received from the respective suppliers. ATP means α -tocopherol.

Code	Composition component	Tradename / Manufacturer
AO-1	component (a)	Irganox 1010/Ciba-Geigy
AO-2	component (a)	Irganox 1076/Ciba-Geigy
PS-1	component (b)	Sandostab P-EPQ/Clariant
ATP	component (c)	Ronotec 201/Hoffmann-La Roche

- 10 The tested samples are prepared as follows. In each case 100 parts of the different types of polyethylenes are dry-blended with the tested additives as well as with a lubricant, followed by pre-extrusion in a single screw laboratory extruder with 80 rpm at temperatures as given below in table 2.
- 15 After extrusion compounding the materials are sequentially passed in total five times through a single screw extruder (compression ratio $\approx 1:3$, $L/D = 20$) at temperatures and numbers of revolutions per minute as given below in table 2. The unstabilized resins are in most cases also processed through the extruder so that all materials have the same heat history. After the five

extrusion passes the materials are assessed in respect of color quality and change of molecular weight.

5 The color quality is reported in terms of the Yellowness Index (YI), determined on the granules in accordance with the ASTM 1925-70 Yellowness Test. The higher the value, the lower the color quality, i.e. the worse the discoloration.

The change of the molecular weight is reported in terms of the melt flow index (MFI) according to ASTM D-1238-70, measured in a Zwick melt flow indexer at temperatures and loads as given below. Experiment errors of the MFI measurements are determined from an independent series of measurements, and are found to be ± 0.01 for the MFI measured at 190°C and 2.16 kg load, and ± 0.3 for the MFI measured at 190°C and 21.6 kg load.

Comparison data refers to the following prior art documents (D):

Code	Document
D-1	Gächter, Müller, Plastics Additives, 3rd edition, Hanser Publishers 1990
D-2	Journal of Plastic Film & Sheeting, volume 11, 1995, pages 126-142
D-3	US P 4,806,580
D-4	EP-A-0 542 108

TABLE 2

Additional conditions of the sample preparations.

Example No.	Type of PE	Lubricant	Compounding temperature	Extrusion	
				temp.	rpm
1	PE-1	500 ppm Zn Stearate	200°C	220°C	70
2	PE-1	500 ppm Zn Stearate	200°C	240°C	70
3	PE-2	1000 ppm Ca Stearate	210°C	270°C	100
4	PE-3	1000 ppm Ca Stearate	210°C	240°C	70

EXAMPLE 1

Comparison data (CD) CD-1 presents the stabilization system according to the currently used formulation.

CD-2 presents the system described in D-2.

CD-3 corresponds to the disclosures given in D-3 and D-4.

I-1 is an example according to the present invention.

As is evident from the results given in table 3, the stabilizer composition according to the invention offers significantly better melt stabilization than systems according to the prior art, providing simultaneously an excellent color retention. The unstabilized polymer (PE-1) illustrates the effect of pronounced crosslinking after 5 repeated extrusions; the MFI drops to the undesirable value of 9.96 g / 10 min.

TABLE 3

Data of example 1.

Experiment	AO-1	PS-1	ATP	MFI		YI
	[ppm]	[ppm]	[ppm]	[190°C/2.16 kg]	[190°C/2.16 kg]	
PE-1	---	---	---	0.05 g / 10 min	9.96 g / 10 min	1.23
CD-1	500	500	---	0.16 g / 10 min	15.79 g / 10 min	-0.6
CD-2	500	---	100	0.15 g / 10 min	15.79 g / 10 min	0.57
CD-3	---	500	100	0.11 g / 10 min	13.06 g / 10 min	0.95
I-1	500	500	100	0.2 g / 10 min	17.43 g / 10 min	-0.55

EXAMPLE 2

Comparison data CD-1 to CD-4 describe common formulations of polyethylene.

CD-5 and CD-6 correspond to the additive systems described in D-2.

CD-7 and CD-8 correspond to the systems disclosed in D-3.

I-1 to I-4 are stabilizer compositions according to the invention.

As can be seen from the results summarized in table 4, the unstabilized polymer is significantly crosslinked after the 5 extrusions. Further, the stabilizer compositions according to the invention significantly outperform the systems known in the art with regard to the melt flow retention and color stabilization. The comparison of the results of CD-3 with those of I-1 on the one hand and of the results of CD-4 with those of I-2 on the other hand clearly demonstrate that the obtained stabilization effect is not caused by an increase of the total concentration of phenolic antioxidant (AO-1 and ATP). It is believed that the stabilization performance of the stabilizer compositions according to the invention, i.e. I-1 and I-2 in the aforementioned comparison, is achieved by a synergistic action of all three components of the stabilizer composition and, thus, cannot be regarded as pure additive, i.e. quantity depending effects. Since the effectiveness of the single components AO-1, PS-1 and ATP is well known in the prior art, it is surprising to find this particular synergy by triple-combinations according to the present invention.

TABLE 4

Data of example 2.

Experiment	AO-1	PS-1	ATP	MFI		YI
	[ppm]	[ppm]	[ppm]	[190°C/2.16 kg]	[190°C/2.16 kg]	
PE-1	---	---	---	0.01 g / 10 min	9.10 g / 10 min	---
CD-1	500	750	---	0.17 g / 10 min	16.76 g / 10 min	-1.00
CD-2	500	1000	---	0.20 g / 10 min	18.03 g / 10 min	-1.10
CD-3	750	750	---	0.17 g / 10 min	17.01 g / 10 min	-0.11
CD-4	750	1000	---	0.20 g / 10 min	18.21 g / 10 min	-0.24
CD-5	500	---	100	0.14 g / 10 min	15.70 g / 10 min	-0.39
CD-6	750	---	100	0.15 g / 10 min	16.33 g / 10 min	-1.14
CD-7	---	750	100	0.14 g / 10 min	14.49 g / 10 min	0.59
CD-8	---	1000	100	0.16 g / 10 min	15.46 g / 10 min	0.42
I-1	500	750	100	0.21 g / 10 min	18.16 g / 10 min	-0.90
I-2	500	1000	100	0.23 g / 10 min	18.98 g / 10 min	-1.10
I-3	750	750	100	0.22 g / 10 min	18.55 g / 10 min	-1.61
I-4	750	1000	100	0.24 g / 10 min	19.10 g / 10 min	-1.67

EXAMPLE 3

CD-1 and CD-2 are comparison tests. I-1 is according to the invention. The results are summarized in table 5.

Again, the stabilizer composition according to the invention gives the best melt and color stabilization. The comparison of the results of CD-2 or CD-3 with those of I-1 repeatedly appears to confirm that the stabilization effect is achieved by a synergistic effect of all three components of the stabilizer composition according to the invention.

TABLE 5

Data of example 3.

Experiment	AO-1 [ppm]	PS-1 [ppm]	ATP [ppm]	MFI [190°C/10 kg]	YI
PE-2	---	---	---	4.83 g / 10 min	---
CD-1	1000	---	---	3.97 g / 10 min	2.8
CD-2	500	1000	---	2.86 g / 10 min	2.7
I-1	400	1000	100	2.55 g / 10 min	1.4

EXAMPLE 4

CD-1 and CD-2 are comparison tests. I-1 is according to the invention. The results are summarized in table 6.

As can be seen from table 6 the stabilizer composition according to the invention conferred unexpectedly outstanding melt flow retention and color stabilization to the tested polymer. This stabilization effect is achieved at a significantly lower total stabilizer concentration than it was used in CD-2.

TABLE 6

Data of example 4.

Experiment	AO-2 [ppm]	PS-1 [ppm]	ATP [ppm]	MFI [190°C/2.16 kg]	YI
CD-1	700	---	---	0.82 g / 10 min	3.0
CD-2	700	1000	---	1.25 g / 10 min	0.2
I-1	250	1000	100	1.30 g / 10 min	-0.8